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(19)



(54) CHEMICAL MODIFICATION OF STARCHES

(71) We, SCHOLTEN - HONIG RESEARCH B.V., a Dutch Body Corporate, of P.O. Box 1, Foxhol, the Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the chemical modification of starch in dry condition and to products obtained thereby.

It is known to modify starches in dry condition by treatment in the presence of starch modifying agents such as dextrinising agents, oxidizing agents, esterifying and etherifying agents. The water content of the starch reaction mixture in such earlier described treatments ranges from about 20% by weight to practically none. ~~Often the presence of 5-20% moisture based on starch is essential for the desired modification reaction.~~

It is also known to treat starch and starch containing products by subjecting them to microwave radiation for the purpose of heating and/or drying. However, in these known processes for microwave radiation a minimum moisture content of the starch product of about 10% by weight is maintained. In the application of microwave radiation for the preparation of quick-cooking rice products and for the drying of pasta products—as in the manufacturing of macaroni—the water content is sufficient to allow swelling and/or gelatinizing of the starch granules during this treatment.

In contradistinction of the known state of the art it has now been found that it is possible to modify chemically and to derivatise starch, by subjecting a starch reaction mixture at a moisture content of less than 10% by weight to microwave radiation without the occurrence of charring, thereby giving modified starches of superior properties in high yield. According to the present invention, therefore, there is provided a process for the chemical modification of starch in dry condition, which comprises subjecting a mixture of starch and of one or more modifying agents which effect a chemical transformation of the

~~starch molecules to microwave energy under such conditions that the water content during the radiation treatment is or reduces to less than 10% by weight of the starch.~~

The term “dry condition” as used in this specification means that less than 20% moisture is present based on the weight of the starch. The process according to the invention makes now available the advantages of microwave heating over the conventional heating methods for modification of starch in dry condition. The conventional heating methods are based on the heat transfer by conduction and convection, and requires a temperature gradient in and between the substances to be heated. Thus the conventional heating methods, for example carried out with heat-exchange surfaces and/or introduction of a hot gas, result in long heating times, as well as local overheating because of which side reactions and pyrolysis of the starch occur. These drawbacks occur especially during the heating of the starch material to high temperatures, i.e. temperatures above 150°C.

We have discovered that for the chemical modification of starch not only a more efficient and faster heating is effected, but also high conversion rates and short reaction times can be achieved. Reaction times of ~~some hours~~ can be reduced to less than about ten minutes by application of microwaves. Besides, higher yields and less contaminated products are obtained by subjecting the starch reaction mixture to microwaves. It is also possible to perform new chemical modifications of starch, which were not known before. The advantages of the novel process are in particular obtained when the starch is modified in particulate form i.e. in the form of segregated particles, thus promoting the removal of moisture. ~~It has been observed that at a moisture content of the starch below 2% by weight a rapid conversion takes place in esterification and etherification modifications.~~

In this specification “the chemical modification of starch” is intended to mean the conversion of starch in the presence of starch modifying agents and optionally of substances accelerating the modification reaction which

will effect dextrinization, hydrolysis, oxidation, derivatisation (etherification or esterification or acetalization) or graft polymerisation of the starch.

- 5 Suitable starches for the chemical modification of starch according to the invention are potato starch, corn starch, wheat starch, tapioca starch, sorghum starch, waxy maize starch, and waxy sorghum starch.

- 10 Instead of pure starch, also protein containing starches can be used, such as flours. The used starch may be in its natural original granular form or may be gelatinized or pretreated. The pretreatment may include chemical conversion such as dextrinization, hydrolysis, oxidation or derivatisation, enzymatical conversion and physical treatments.

- 15 Suitable agents for chemical modification according to the invention are the commonly known modifying agents which effect dextrinization, oxidation, derivatisation or graft polymerisation of the starch as described in Radley "Starch and its Derivatives", 1968 Chapman and Hall Ltd. Chapter 11 and 12; Whistler/Paschall "Starch: Chemistry and Technology" Academic Press. Volume I (1965) Chapter XVIII and XIX; Volume II (1967) Chapters IX, X, XI, XIII, XIV, XV, VI, XVII, XIX.

- 30 Examples of chemical modifications according to the invention and suitable modifying agents are the following:

- 35 Dextrinisation in the presence of agents such as hydrochloric acid, nitric acid, aluminum chloride, trisodium orthophosphate and other agents.

- 40 Oxidation in the presence of nitrogen dioxide, chlorine, hypochlorite, sodium perborate, ammonium persulfate, hydrogen peroxide and other oxidising agents.

- 45 Hydrolysis and/or esterification modification of starch in the presence of inorganic acids and/or salts thereof—optionally in combination with other agents—such as sulfuric acid, hydrochloric acid, nitric acid, sulfamic acid, ortho phosphoric acid, pyro phosphoric acid and polyphosphoric acid and organic acids such as acetic acid, lauric acid and citric acid, alkali and ammonium salts of phosphorus containing acids, such as ortho phosphate salts, pyrophosphate salts, metaphosphate salts, polyphosphate salts and mixtures thereof, optionally in combination with amines, amides and ammonium compounds, complexes of sulfur trioxide with tertiary amines, mixtures of sodium bisulfite and sodium nitrite.

- 50 Derivatisation with known monofunctional or polyfunctional etherifying and esterifying agents, for example monofunctional etherifying agents such as alkylhalides, halogenated carboxylic acids, epoxy alkanes, dialkylsulphates, alkane sultones, acrylonitrile, acrylamide, acrylic acid esters and the like, monofunctional esterifying agents such as carboxylic acids, carboxylic acid anhydrides, carboxylic

acid chlorides, vinyl esters of carboxylic acids, lactones, ammonium salts of carboxylic acids, urea, aliphatic or aromatic monoisocyanates and polyfunctional agents such as epichlorohydrin, phosphorus-oxychloride, polybasic acid anhydrides, diisocyanates, aldehydes, synthetic resin precondensates. These derivatisations can be carried out in the presence of acid, alkaline or neutral substances which accelerate the reactions.

Graft polymerisation of starch with acrylic compounds such as acrylic acid, sodium acrylate, acrylonitrile, acrylamide are performed in the presence of catalyst systems, such as hydrogen peroxide-ferrous ion and persulfate-bisulfate combinations.

The dry reaction mixtures of starch and modifying agents suitable for the process of chemical modification according to the invention can be obtained in various manners. For instance air dry starch may be sprayed with an aqueous solution of the modifying agent.

It is also possible to mix moist starch (moisture content about 35–40% by weight) and the modifying agents followed by drying of the mixture. Alternatively the starch may be suspended in an aqueous solution or suspension of the modifying agents and after stirring and collecting on a filter, it may be dried. In all cases the mixture should be adjusted to a moisture content below about 20% by weight of the starch.

The drying can be carried out with common drying apparatus such as e.g. pneumatic dryers or rotating drum dryers.

To be suitable for the chemical modification according to the invention the starch reaction mixture should have or should reach a moisture content of less than 10% by weight during the microwave radiation. We have made the observation that when a mixture with a moisture content above 10% is subjected to microwaves without evaporation of water hardly any conversion will take place or unstable and strongly coloured products are obtained. However, starch reaction mixtures with a moisture content above 10% by weight of the starch can favourably be used as starting material for the process according to the invention provided reaction conditions are chosen which promote the evaporation and removal of moisture from the mixture. It has been found, that when a starch reaction mixture with a moisture content above 10% by weight of the starch is subjected to microwave energy under said reaction conditions, broadly the following will happen:

In the first phase of the process the warming up of the starch and evaporation of water prevails, while the temperature will rise to about 110°C. In the subsequent phase of the process when the moisture falls below about 10% by weight, along with continuing lowering of the moisture content the conversion starts and at last a very rapid conversion

takes place at temperatures reaching 140°C and higher.

5 To promote uniform removal of moisture and uniform heating it is desirable to keep the reaction mixture in agitation, for instance in a rotating drum or in a stationary chamber with agitation. Alternatively a gas stream can be passed through or over the mixture.

10 A preferred procedure is fluidisation of the starch reaction mixture. In fluidisation a bed of finely divided particles is lifted and agitated by a rising stream of gas.

Fluidisation can be achieved by feeding the gas uniformly through a bed of particles, 15 for example, by using a column with a gas distributing bottom plate. A fluidised bed results. A variant is formed by penetration of a jet of gas through a bed of particles. This can be carried out by feeding the stream of gas centrally into a column with a conical bottom. A spouted bed is formed which has a channel in the centre and does not have a homogeneous distribution of particles throughout the bed. Also included are beds consisting 20 of dense liquid-like suspension of turbulent solids, which are established by transmitting an oscillating motion generated by mechanical means to the mass of solids. Gases such as air, nitrogen or carbon dioxide may be passed through such beds at velocities lying below the level necessary to give fluidisation by the gas alone. All these types of fluidised beds are suitable for the process according to the invention.

35 Thus it is a preferred embodiment of the process according to the invention to subject a fluidised mixture of starch and modifying agents to microwave radiation. For fluidisation the mixture must be powdered or granular and have a maximum moisture content of about 40 15—20% by weight of the starch. To enhance the fluidisability, substances which improve the mobility of the mixture may be added in minor quantities (0.1—2% by weight based on starch). Examples of these substances are tricalcium phosphate, magnesium oxide or colloidal silica. Air, nitrogen, carbon dioxide or mixtures thereof are suitable as fluidisation gases. When the modifying agents 50 are gaseous or volatile substances, they can be applied in admixture with the fluidisation gas.

The microwaves suitable for application in the process according to the invention are 55 electro magnetic waves having frequencies ranging from 300 MHz to 300,000 MHz.

The frequency can be selected in relation to several variables such as the dielectric properties of the material and the dimensions of the reactor. For industrial applications, however, only certain specific frequency bands are permitted by the authorities in several countries. These frequency bands include 915, 2450, 5800 and 22155 MHz. In practice these 65 frequencies will be applicable in the process

according to the invention. The invention is, however, not limited to these frequencies.

The chemical modification of starch according to the invention can be performed in every known type of microwave processing 70 apparatus. A microwave processing apparatus normally includes a microwave generator in the form of a magnetron or klystron, an applicator in the form of an enclosure, which confines the microwaves and in which the 75 materials are exposed to microwaves and wave guides, which interconnect the generator and applicator, for transport of the microwave energy.

The construction of microwave processing 80 apparatus, the dimensions of the wave guides and applicators, special forms and means for applicator chambers for preferred modes of propagation, directing or focussing on specific regions of the chamber, and suitable 85 materials of construction are generally known. The applicator may be adapted to batch-wise or continuous procedures. So the applicator may be a chamber in which the material can be placed for exposure to microwave in a 90 holder, which is transparent for microwaves e.g. a pan or a column for a fluidised bed. Further the chamber may be provided with inlet and outlet openings to pass the material through the chamber by conveyor belt or 95 pneumatically. It is also possible to construct the applicator in the form of a rotating drum or of a column for holding a fluidised bed (compare: G. B. Allen: The Journal of Microwave Power 3 p. 23). At the same 100 time the applicator may be provided with a system to maintain a vacuum or a specific gas atmosphere. Optionally the microwave processing apparatus may include various 105 monitoring devices for measurement of process conditions such as dryness or temperature of the treated material. For the preferred embodiment of the process according to the invention, in which a fluidised starch reaction mixture is subjected to microwaves, a microwave 110 confining chamber in the form of a column holder for a fluidised bed is favoured. Especially for conversion at temperatures above 150° C the heating of the fluidised material by microwaves is advantageous in comparison 115 with conventional methods of heating with heat-exchanging surfaces inside the fluidised bed. These advantages are: no over heating at heat-exchanging surfaces, no need for internal heat-exchanging surfaces thus leaving more 120 free space inside the column holder for material to be treated, less surface exposed to the abrasive action of fluidised particles; less blind spots, which cause contamination of the product by withholding material of prior charges 125 and fast control of the heating system. Although subjecting a starch reaction mixture to microwave radiation in fluidised bed, is the preferred embodiment of the process the invention is not limited thereto. 130

The efficiency and advantages of the chemical modification of starch by subjecting to microwaves appear in all embodiments of the process.

- 5 Because of the great number of variables in performing the process according to the invention such as the input of microwave energy into the material, the composition of the reaction mixture, the modifying reaction, the used microwave confining chamber, the desired reaction time, the used microwave frequency it is only possible to give general parameters. More definite parameters can easily be determined experimentally by carrying out some process variations for a specific modification reaction. In this way it is possible, for instance, to determine the optimum conversion time, which is usually in the order of less than 10 minutes. These conversion times are much shorter than can be expected on account of high temperature or the efficiency of heating alone.

- 10 In the process according to the invention less contaminated modified starch products are obtained more efficiently, in shorter reaction times and higher yields than in the conventional processes. The following examples illustrate the invention.

Example I

- 30 This example describes the dextrinisation of starch in the presence of hydrochloric acid by subjecting the predried mixture to microwaves. For this purpose potato starch is acidified to pH 2.45 by spraying with 1 N hydrochloric acid.

35 In 2 hours the mixture is dried in a rotating drum at 110°C to a moisture content of 0.9% by weight.

- 40 To the mixture an amount of 2.01% by weight of colloidal silica is added to enhance the fluidity.

- A sample of this mixture is fluidised by a stream of air in a fluidisation column placed in a microwave processing apparatus. The apparatus is "Microwave Heating System" type MH 1500/50 of Rotax Ltd. This apparatus consists of a magnetron, which is connected by wave guides with a microwave confining chamber. The magnetron generates microwaves with a frequency of 2450 MHz and has a maximum power output of 1.5 KW.

- 50 At a current of 200 mA of the magnetron the dextrinisation takes 5 minutes. The dextrin so obtained has an Ostwald viscosity of 34.7 cps and a Hellige colour of 12. At a current of 100 mA of the magnetron dextrinisation is achieved in 10 minutes. The dextrin thus ob-

tained has an Ostwald viscosity of 36.3 cps and a Hellige colour of 12.

Conventional dextrinisation, which yields dextrins with an Ostwald viscosity of 34—38 cps which have an Hellige colour of at least 13, requires a dextrinisation time of 3—4 hours. The stability of dextrins prepared by the microwave method is better than the stability of conventional dextrins of corresponding Ostwald viscosities.

When a predried mixture is dextrinised in a rotating container of glass placed in the microwave chamber, the dextrinisation time amounts to 2-1/2 minutes at a current of 300 mA of the magnetron. The dextrin so obtained has an Ostwald viscosity of 27.1 cps and a Hellige colour of 10. The Hellige colour is determined by comparing the colour of a solution obtained by cooking dextrin with a moisture content of 13% by weight in water (1:1 by weight) during 15 minutes, with a Standard colour scale of Hellige. A higher value of Hellige colour means stronger colouration. The Ostwald viscosity is determined with an Ostwald viscosimeter. For that purpose a solution of dextrin is prepared by stirring 1 part by weight of dextrin with a moisture content of 13% by weight in 1.5 parts by weight of water and heating during 1 hour at 70°C.

After cooling and correcting the weight for evaporated water, the solution is filtered through a silk gauze before determination of the viscosity.

Example II

This example describes the modification of starch in the presence of phosphoric acid and urea.

A mixture is prepared by mixing 2500 parts by weight of potato starch, 150 parts by weight of phosphoric acid (85%) and 375 parts by weight of urea dissolved in 200 parts by weight of water and acidified with 10 N sulfuric acid to pH 1.43, in a Herfeld mixer during 60 sec. at 1200 r.p.m. After drying in a pneumatic dryer a mixture is obtained of potato starch with 6% by weight of phosphoric acid, 15% by weight of urea and a moisture content of 10% by weight of the starch.

To enhance the fluidity 0.15% by weight of colloidal silica is added calculated on the starch.

Samples of this mixture are subjected to microwaves in fluidised state as described in Example I during which treatment the moisture content drops below 10% by weight. The following results are obtained:

	Current of magnetron	Reaction time sec.	Viscosity cps	Bound P205 %	Yield %	Whiteness %
	120 mA	2	49.0	1.75	40.2	70.0
	120 mA	4	49.6	2.38	54.7	64.0
5	200 mA	2.5	52.0	2.92	52.6	67.0
	280 mA	1.5	28.0	1.72	39.5	69.5
	200 mA	3	4066	3.66	84.1	
	120 mA	5	11760	3.94	90.6	

The viscosity is measured with a Brookfield HAT viscosimeter at 50°C in an aqueous solution of 15% by weight. The phosphorus content is determined according to the method of Allen (R.J.L. Allen: Bioch. J 34 858—865 (1940)). The whiteness is determined by comparing the whiteness of a dry product with that of magnesium oxide in a spectrophotometer and expressing the result in % whiteness.

For comparison starch phosphates obtained by modifying in fluidised bed using internal heat-exchanges require 1—3 hours reaction time, while the yields are about 40%. To obtain starch phosphates with a viscosity of 20—60 cps and a whiteness of 60—70% the process of the invention requires much shorter reaction times and gives the same or higher yields, as can be achieved by the conventional process. For starch phosphates with a higher phosphate content much higher yields are achievable with the new process.

Example III.

This example describes the etherification with sodium monochloroacetate. 200 parts by weight of potato starch and 116.5 parts by weight of sodium monochloroacetate, dissolved in 350 parts by weight of water are mixed in a Herfeld mixer in 60 seconds at 1200 r.p.m. After drying in an oven at 40—50°C during 18 hours to a moisture content of 15% by weight and adding colloidal silica to enhance the mobility, the mixture is fluidised and subjected to microwaves as described in example I during which treatment the moisture content drops below 10% by weight.

At a current of 120 mA of the magnetron the radiation takes place during 10 minutes. A product is obtained with a degree of substitution of 0.06. The etherification yield is 58%.

This result is surprising. For this etherification takes place in absence of an alkaline etherification catalyst and under dry conditions. Thus far this reaction has only been accomplished in the presence of an alkaline catalyst.

When after drying of the mixture 1 gram equivalent of powdered sodium carbonate is added a D.S. of .07 and an etherification yield of 73% are achieved.

Example IV

This example shows the course of the chemical modification when the starting mixture has a moisture content above 10% by weight.

For this purpose a mixture of potato starch and 6% by weight of phosphoric acid (85% and adjusted to pH 4.3) is prepared in a mixer in 60 seconds at 1200 r.p.m. The mixture is dried in a pneumatic dryer to a moisture content of 14% of the weight of the starch and colloidal silica is added.

Samples of this mixture are fluidised using air as fluidizing gas and subjected to microwaves as described in Example I. The current of the magnetron is 200 mA.

The reactions of the successive samples are interrupted after 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 minutes, after which the temperature, the moisture content and phosphorus content are determined.

The results are given in Figure 1.

From this figure it can be concluded that in the first phase of the process lowering of the moisture content prevails while in the subsequent phase a rapid conversion takes place. After 10 minutes reaction time the phosphate content is 3.01% as bound P_2O_5 . The yield is 82%.

Example V

In this example the procedure of example IV is repeated for the modification of potato starch with sodium monochloroacetate.

After preparing a mixture of starch and sodium monochloroacetate (0.5 mol/1 kg of starch), having a moisture content of 14% of the weight of the starch and adding colloidal silica, samples of the mixture are subjected to the procedure as described in example IV. The results are given in figure 2. As in example IV for the esterification reaction, an initial lowering of the moisture content is succeeded by a rapid etherification reaction after the moisture content has dropped to less than 2%.

Example VI.

This example describes the modification of starch with sulfamic acid and urea. A mixture is prepared by suspending 2500 parts by weight of corn starch in 3500 parts by weight of water in which 1200 parts of weight of urea and 300 parts by weight of sulfamic acid are dissolved. After removal of water by centrifuging the mixture (40% moisture) is dried during 24 hours in an oven at 40—50°C.

The mixture so obtained has the following

composition potato starch 87% by weight d.s. urea 10.4% weight d.s. sulfamic acid, 2.6 by weight d.s. and moisture 9% of the weight of the starch. The mixture is fluidised and exposed to microwaves as described in Example I. At a current of 200 mA of the magnetron radiation takes place during 3 minutes. The product obtained yields on cooking in water, a low-viscous, clear and stable solution. The content of bound sulfur is 0.86% by weight on dry substance.

When dry reaction mixtures of starch, sulfamic acid and urea are heated with conventional heating methods, the reaction requires 4—5 hours at 130°C. The content of bound sulfur is about 0.75% (see U.S. Patent 2,857,377).

Example VII

This example describes the modification of starch with the ammonium salt of maleic acid. In a Lödige mixer 2000 parts by weight of tapioca starch and 100 by weight of maleic acid dissolved in 300 parts by weight of water and adjusted to pH 7.3 with ammonia (35%), are mixed during 30 minutes at 100 r.p.m. After drying over night in an oven at 40—50°C to a moisture content of 8% by weight and adding colloidal silica, the mixture is modified in a rotating container of glass which has been placed in the microwave apparatus.

Using a reaction time of 5 minutes at a current of 200 mA of the magnetron a cross-linked starch product is obtained. On dissolving in water (1:10 by weight) the product gives a slightly yellow salve-like solution. The product has an acid number of 9.6 mg KOH/g dr.s., a saponification value of 21.1 and esterification number of 11.5 g dr.s. The degree of substitution is 0.03.

Example VIII

This example describes the graft polymerisation of starch with acrylamide.

A mixture of potato starch (moisture content 20% by weight) and acrylamide (10% by weight calculated on starch) are dried to a moisture content of 5% by weight at 70°C. Thereafter 0.3% by weight of colloidal silica and 0.5% by weight of benzoylperoxide are added.

The mixture is fluidised with nitrogen gas and exposed to microwaves as described in Example I using a current of 100 mA of the magnetron during which treatment the moisture content drops below 5% by weight.

A white product is obtained in 2 minutes with a yield of 58%. Corresponding with a nitrogen content of 1.1% by weight. Before

determination of the nitrogen content the graft polymer is washed with water or a water-alcohol mixture to remove unbound nitrogen.

WHAT WE CLAIM IS:—

1. A process for the chemical modification of starch in dry condition which comprises subjecting a mixture of starch and one or more modifying agents which effect a chemical transformation of the starch molecules to microwave energy under such conditions that the water content during the radiation treatment is or reduces to less than 10% by weight of the starch.

2. A process as claimed in claim 1 in which the starch is modified in particulate form thus promoting the removal of moisture from the mixture.

3. A process as claimed in claim 1 or 2 in which a gas is passed through the mixture during exposure to microwave energy.

4. A process as claimed in any of claims 1 to 3 in which the mixture is in a fluidised state.

5. A process as claimed in any one of the preceding claims in which the mixture consists of starch and monochloroacetic acid or the alkali metal salt thereof.

6. A process as claimed in any one of claims 1 to 4 in which the mixture consists of starch, urea and a phosphorus containing acid or the alkali metal or ammonium salts thereof and/or sulfamic acid.

7. A process as claimed in any one of the preceding claims in which said chemical modification is etherification or esterification of starch and in which the microwave energy is supplied to such an extent that the etherification or esterification reaction takes place at temperatures above 120°C. and at a moisture content of the reaction mixture of less than 2% by weight of the starch.

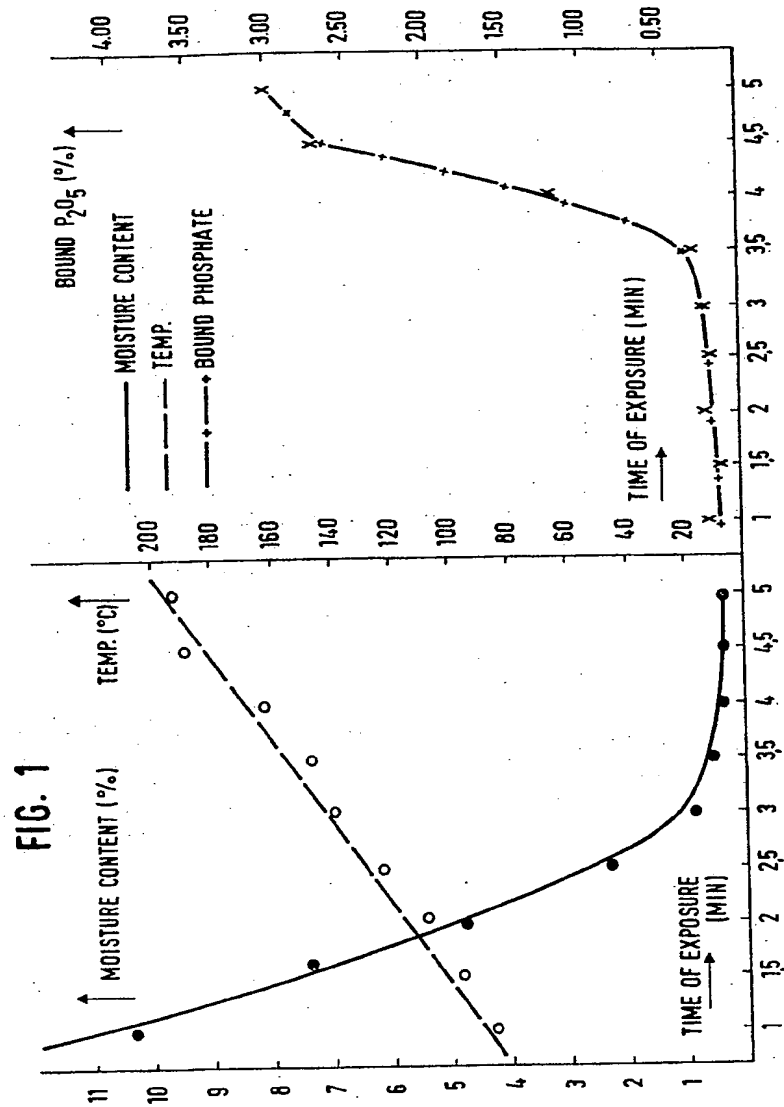
8. A process for the chemical modification of starch in dry conditions as claimed in claim 1 and substantially as hereinbefore described with reference to any one of the foregoing Examples.

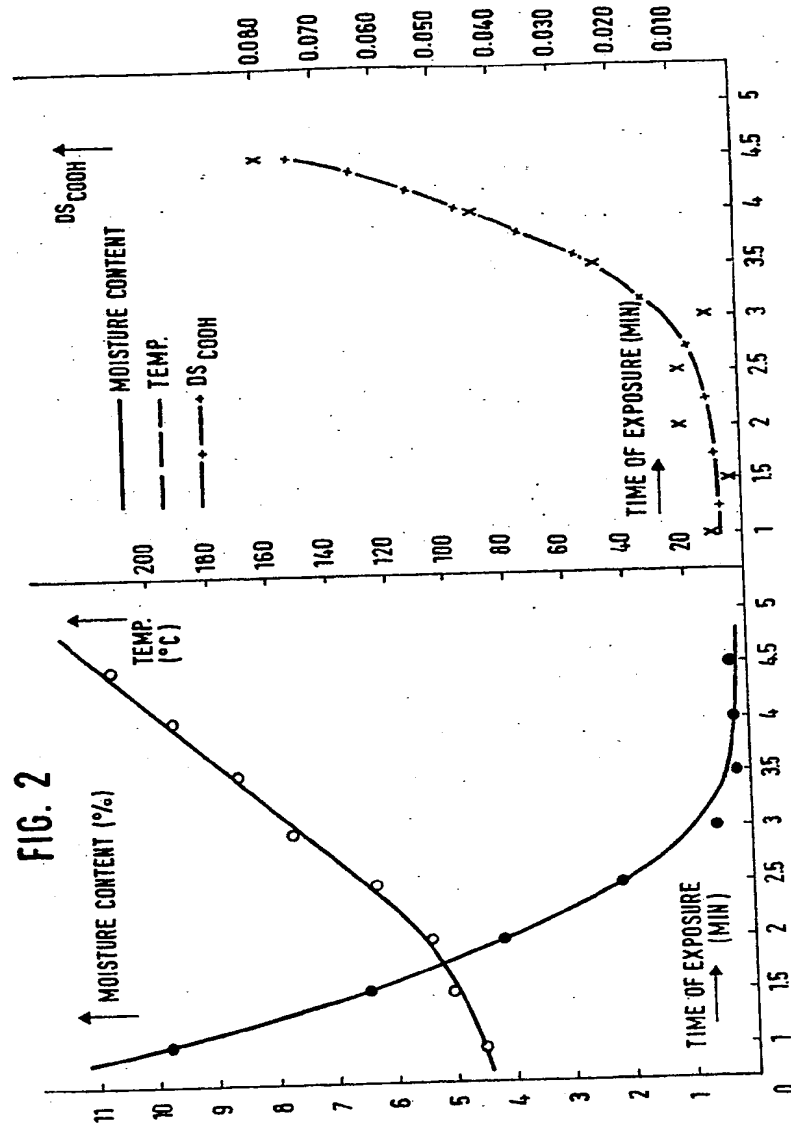
9. A starch modification product obtained by a process as claimed in any one of the preceding claims.

10. A starch modification product as claimed in claim 9 and substantially as hereinbefore described with reference to Example I to VIII.

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